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Mechanistic Aspects of Hydrodeoxygenation of *p*-Methylguaiacol over Rh/Silica and Pt/Silica

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ABSTRACT: The mechanism of *p*-methylguaiacol (PMG) hydrodeoxygenation (HDO) has been examined over two Rh/silica catalysts and a Pt/silica catalyst at 300 °C and 4 barg hydrogen. Sequential conversion of PMG to 4-methylcatechol is followed by *m*- and *p*-cresol formation and finally toluene production, although direct conversion of PMG to *p*-cresol is favored over a commercial Rh/silica catalyst. Dehydroxylation and hydrogenation are shown to occur over metal functions, while demethylation and demethoxylation are favored over the fumed silica support. A mechanistic pathway for HDO of PMG is proposed.

KEYWORDS: *p-methylguaiacol, hydrodeoxygenation, rhodium, platinum, mechanism*

INTRODUCTION

Hydrodeoxygenation (HDO) of bio-oils is an active research area in both catalysis and bioenergy[1,2] and is one of the methodologies capable of upgrading bio-oils into a form suitable for blending with petroleum. Previously[3] we examined the deactivation of three catalysts for HDO of *p*-methylguaiacol (PMG), a common component of pyrolytic bio-oils. The catalysts were 2.5 wt % Rh/silica supplied by Johnson Matthey (JM) and in-house-prepared 2.5 wt % Rh/silica (A) and 1.55 wt % Pt/silica (A). All three catalysts exhibited an initial deactivation phase, although Rh/silica (JM) achieved a steady state after ∼6 h on stream and maintained a constant activity over the subsequent test period. In contrast, the two in-house-prepared catalysts did not reach steady state within the testing time frame: both Rh/silica (A) and Pt/silica (A) underwent continuous deactivation, albeit following different mechanisms.[3] Here we focus on the reaction mechanisms over the different catalysts and their response to deactivation. There are no other literature studies of PMG, but guaiacol has been the subject of several investigations. Mu et al.[4] studied guaiacol HDO over a Rh/C catalyst at 40 bar hydrogen and 250 °C in a batch reactor and reported demethoxylation to be the dominant process, resulting in phenol as the main product (∼35% selectivity) at a modest conversion of ∼13%; other major products were cyclohexanone and cyclohexanol (∼25% selectivity). Gutierrez et al.[5] examined rhodium and platinum on zirconia supports for guaiacol HDO and predominantly observed hydrogenated products at 100 °C with some deoxygenation at 300 °C, although few details were provided. Platinum catalysts have been somewhat more researched, and their HDO mechanism has been considered. A detailed reaction network for guaiacol conversion over Pt/alumina was uncovered by Gates and co-workers,[6] wherein a wide product distribution was detected, reflecting HDO in competition with transalkylation and hydrogenolysis. In the course of our previous work it became apparent that demethylation, demethoxylation, and hydrogenation pathways were affected differently by catalyst deactivation, and we were interested in putting this into context mechanistically and, through the use of two metals and two silica supports, determining the active site for each reaction.

RESULTS AND DISCUSSION

The three catalysts were tested for HDO of PMG over an extended period of 32 h. As previously reported, the Rh/silica (JM) catalyst achieved a steady state within the time frame of the testing, whereas Rh/silica (A) and Pt/silica (A) both exhibited continuous deactivation, resulting in significant selectivity variations between 1 and 32 h on stream (Figures 1−3).

In the early stages of the test, Rh/silica (A) was selective for toluene (33%) and *p*-cresol (30%), but after 32 h time on stream, the major products were 4-methylcatechol (41%) and *p*-cresol (34%). This is in marked contrast to Rh/silica (JM), where the toluene selectivity (<5%) and 4-methylcatechol selectivity (<10%) were both low throughout the test. Pt/silica (A) displayed a less pronounced switchover from *m*- and *p*-cresol to 4-methylcatechol production.

Mechanistically, the results for both Rh catalysts reflect sequential hydrogenolysis reactions, as shown in Scheme 1. As Rh/silica (A) deactivates, it loses hydrogenolysis/HDO activity, such that the demethylation product 4-methycatechol is increasingly favored. This selectivity switching mirrors the relative ArO−CH_3 versus Ar−OCH_3 bond strengths of ∼381 versus 419 kJ mol^{-1}, respectively. None of the catalysts

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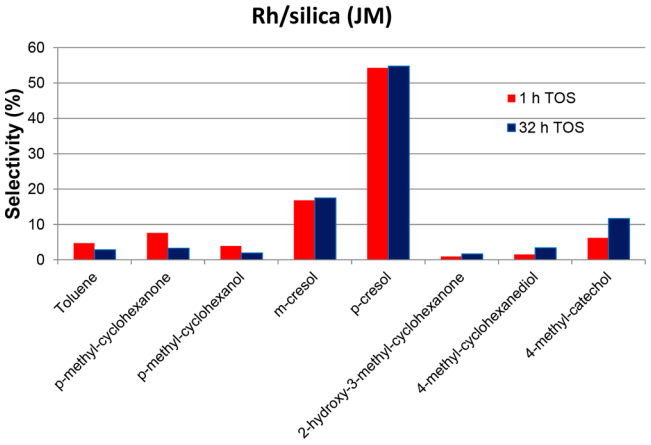


Figure 1. Product distribution for *p*-methylguaiacol HDO over Rh/silica (JM). The conversion was 47% and 34% after 1 and 32 h time on stream, respectively.

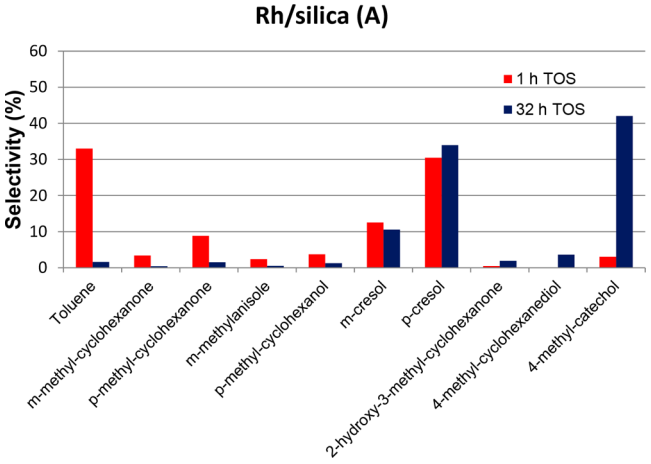


Figure 2. Product distribution for *p*-methylguaiacol HDO over Rh/silica (A). The conversion was 50% and 26% after 1 and 32 h time on stream, respectively.

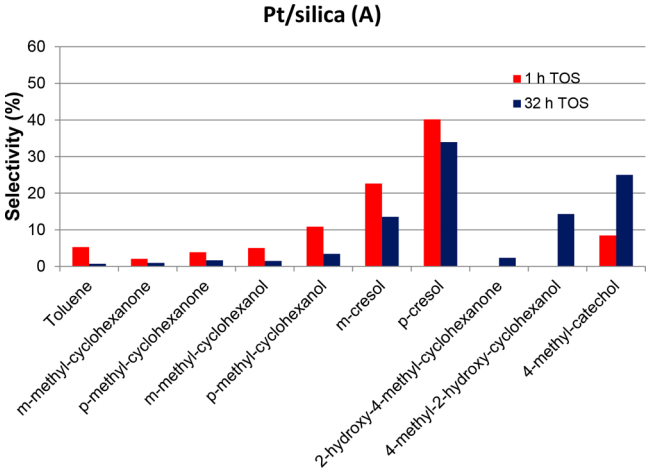
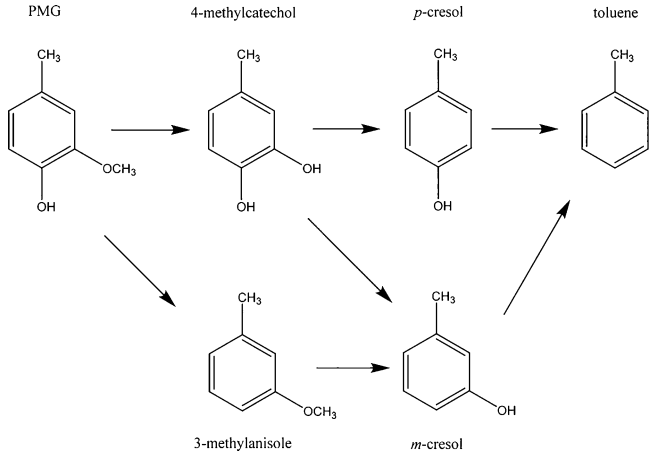


Figure 3. Product distribution for *p*-methylguaiacol HDO over Pt/silica (A). The conversion was 70% and 47% after 1 and 32 h time on stream, respectively.

promoted C−C bond scission and concomitant benzene generation, and only products of cresol hydrogenation (*p*- and *m*-methylcyclohexanone) were observed, but not methylcyclohexane. 3-Methylanisole was formed only as a minor product over Rh/silica (A), suggesting that dehydroxylation of PMG to 3-methylanisole (and subsequent demethylation to *m*-cresol) is generally an unfavorable pathway, consistent with its high energy barrier of ~431 kJ mol^{-1}. Demethylation of PMG to 4-methylcatechol was unaffected by deactivation, presumably reflecting the weaker bonds to be cleaved. *p*-Cresol may form by either direct demethoxylation of PMG or (very energetically unfavorable) dehydroxylation of 4-methylcatechol. Since *p*-cresol production was largely unaffected by deactivation, we conclude that it forms through the former (less energy-intensive) direct demethoxylation. Rh/silica (JM) is never effective for complete PMG dehydroxylation (toluene selectivity <5%), indicating a lack of the highly active sites requisite for such a challenging bond cleavage, which may in part underlie its superior stability. To test the proposed mechanism, the catalyst was operated under a range of space velocities. As the space velocity was increased, the conversion and selectivity for secondary products decreased, but the selectivity for 4-methylcatechol increased (the yield also increased, except at the highest space velocity), as shown in Figure 4, confirming 4-methylcatechol as a primary product.

Scheme 1. Mechanism of Hydrogenolysis/HDO of PMG



Although the major products over Pt/silica (A) after 1 h time on stream were *m*-cresol and *p*-cresol, there was also marked hydrogenation activity, as evidenced by significant selectivity for hydrogenated cresols. The initial total selectivity

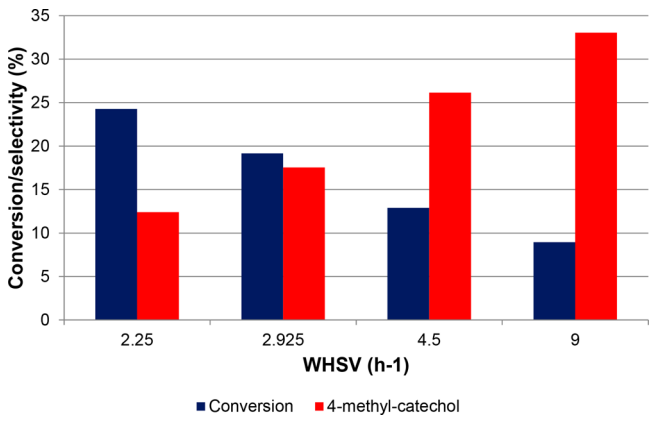


Figure 4. Conversion of PMG and selectivity for 4-methylcatechol. Conditions: 280 °C, 4 barg H_2.

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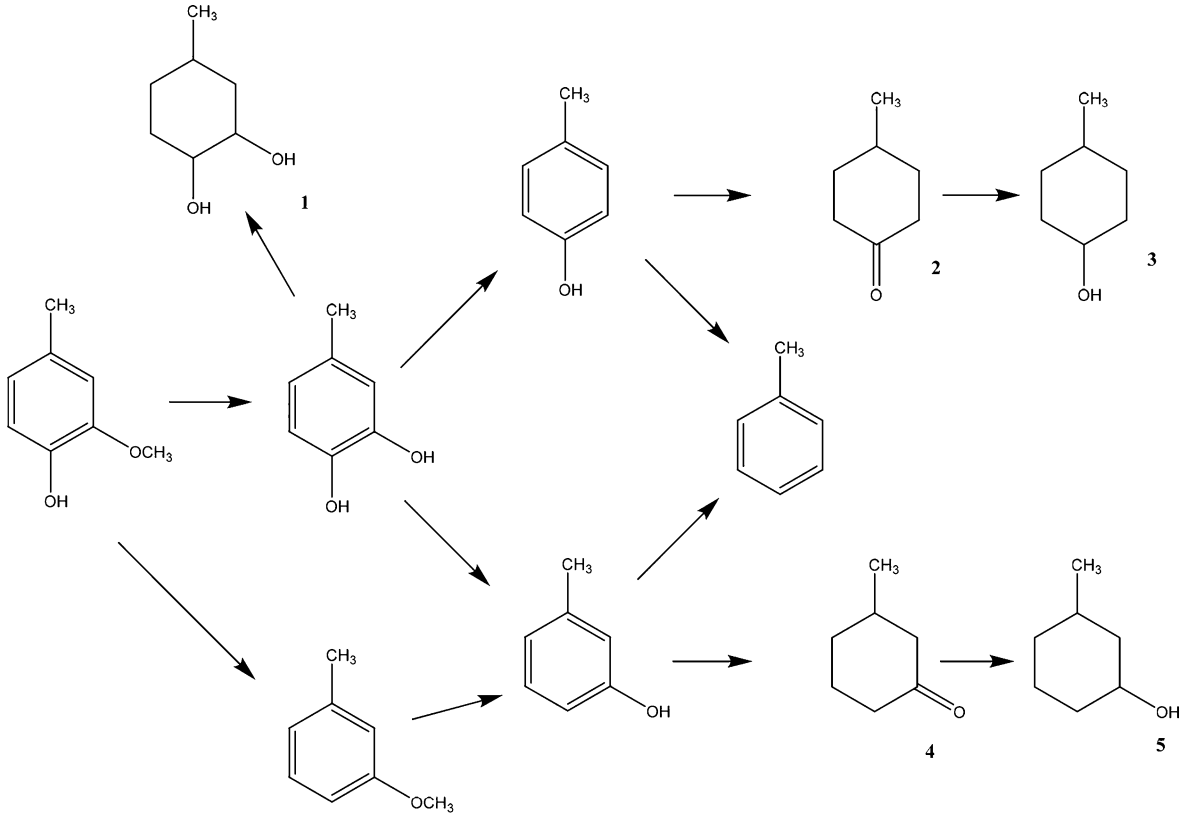
Scheme 2. Extended Mechanism of Hydrogenolysis/HDO/Hydrogenation of PMG[a]



[a]The aromatic species are as in Scheme 1. Compound **1**, 1,2-dihydroxy-4-methylcyclohexanol; compound **2**, 4-methylcyclohexanone; compound **3**, 4-methylcyclohexanol; compound **4**, 3-methylcyclohexanone; compound **5**, 3-methylcyclohexanol.

for *p*-methylcyclohexanone and *p*-methylcyclohexanol was ~11% (with proportionally lower values for the meta isomers). After 32 h, when the catalyst had deactivated, the selectivity changed to favor 4-methylcatechol and the hydrogenated form 4-methyl-2-hydroxycyclohexanol. Overall, Pt/silica (A) is the most active hydrogenation catalyst, which is maintained even during deactivation.[3] The mechanism outlined in Scheme 1 can be extended to give Scheme 2 that takes into account the platinum hydrogenation activity.

The above discussion considers the behavior of the catalysts with time and changes in their selectivities; however, it is also worthwhile to compare the selectivities at equivalent conversion. The results are shown in Figure 5. What is immediately noticeable is that the yield/selectivity for 4-methylcatechol is the same for both Rh/silica (A) and Pt/silica (A), the catalysts with the same support. This suggests that the demethylation reaction (breaking of the ArO−CH_3 bond) is favored over the fumed silica support rather than the metal function. In contrast, dehydroxylation (breaking of Ar−OH bonds) appears to take place over the metal function. This is suggested by the selectivity for toluene, where the Rh catalysts give a similar figure, but is confirmed by the selectivity for *m*-cresol and *m*-anisole (Rh/silica (JM) and Rh/silica (A) selectivity = 0.6%, Pt/silica (A) selectivity = 0.4%). This in agreement with the results reported by Nimmanwudipong et al.,[6] who suggested that dehydroxylation was performed over the metal function. It is also consistent with the deactivation study, where the demethylation activity was the least affected by carbon deposition.[3] There are two routes to the formation of *p*-cresol: through 4-methylcatechol by dehydroxylation and direct from PMG by demethoxylation. In view of the fact that dehydroxylation is a difficult process, the high selectivity for *p*-cresol over Rh/silica (JM) suggests that demethoxylation of PMG to give *p*-cresol takes place over the support.

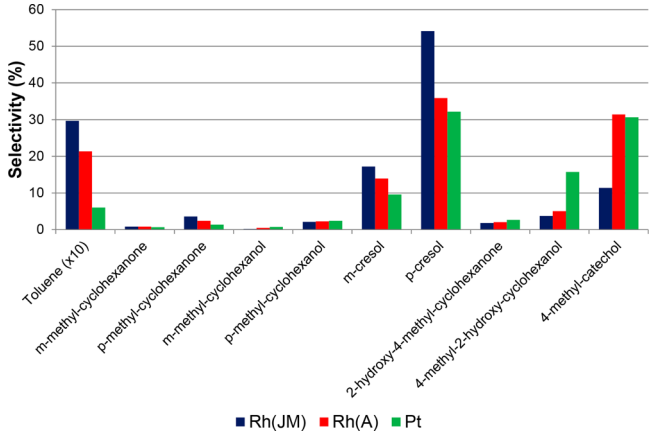


Figure 5. Selectivities for various products at ~32% conversion.

In conclusion, we have clarified and simplified the mechanism for PMG hydrodeoxygenation and hydrogenation. Dehydroxylation and hydrogenation have been shown to occur over metal functions, while demethylation and demethoxylation are favored over the fumed silica support. Only one catalyst (Rh/silica (A)) gave significant yields of toluene, the full HDO product, but the sites responsible were rapidly deactivated. Overall, rhodium was a more effective HDO metal than platinum.

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EXPERIMENTAL SECTION

Three catalysts were used in this study: 2.5% Rh/silica (JM), 2.5% Rh/silica (A), and 1.55% Pt/silica (A). All of the catalysts were prepared by impregnation, and details of their preparation are reported elsewhere.[3] The catalysts were ground and sieved to between 350 and 850 μm before use, and all reagents and solvents were purchased from Sigma-Aldrich and used without further purification.

The conversion, selectivity, and yield are defined in eqs 1, 2, and 3, respectively:

$$\text{conversion} = \frac{\sum \text{moles of products}}{\sum \text{moles of products} + \text{moles of PMG out}} \quad (1)$$

$$\text{selectivity} = \frac{\text{moles of product}}{\sum \text{moles of products}} \quad (2)$$

$$\text{yield} = \frac{\text{moles of product}}{\sum \text{moles of products} + \text{moles of PMG out}} \quad (3)$$

The catalytic testing methodology has been reported elsewhere.[3] Briefly, the tests were performed in a continuous-flow fixed-bed reactor. The catalysts (~0.5 g) were prereduced in situ before reaction at 300 °C for 2 h under a 100 mL min^{-1} flow of 40% H_2/Ar. After the catalysts were reduced, PMG was pumped into the gas flow and vaporized at 200 °C. The reaction temperature was 300 °C with a hydrogen partial pressure of 4 barg, giving a H_2:PMG ratio of 15. The total pressure was made up to 10 barg using argon. The typical weight hourly space velocity (WHSV) of PMG was 2.5 h^{-1}, while the gas hourly space velocity (GHSV) was 7200 h^{-1}. The products were trapped in a condenser at 5 °C before sampling.

A full description of the analysis methodology has been reported elsewhere.[3] In brief, to fully quantify the products, three distinct solutions were prepared from the same mixture of products. First two internal standards were added (decane at 0.86 g L^{-1} and heptadecane at 10.2 g L^{-1}), and then two aliquots were silylated. Analysis of the three solutions using this technique permitted full quantification of the minor and major products. The quantitative analyses were performed on an HP 5890 gas chromatograph fitted with a Supelco DB-5 capillary column (30 m × 0.32 mm, 1 mm thickness).

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Notes

The authors declare no competing financial interest.

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